APPENDIX G

SAMPLING PROTOCOL CONSIDERATIONS

Developing a Consistent Sample Collection Protocol

A good field sampling protocol incorporates eight basic elements:

1. Where to collect samples
2. When to collect samples
3. Sample bottle preparation
4. Sample collection technique
5. Storage and preservation of samples
6. Sample labeling and chain of custody plan
7. Quality assurance/control samples
8. Safety considerations

1. Where to Collect Samples

Indicator sampling normally occurs at three principle locations in the storm drain system to detect illicit discharges - at the outfall, in the stream, and within the storm drain pipe network.

Monitoring of dry weather flows from outfalls is the most common location in most IDDE programs, and the majority of this chapter focuses on these techniques.

In-stream monitoring involves sample collection at perennial stream channels during dry weather flow conditions. Stream monitoring is less precise than outfall monitoring at detecting individual discharges. It can, however, screen stream reaches for those with the greatest illicit discharge potential, detect the most severe or high volume discharges, and measure progress over time in terms changes in stream water quality.

In-pipe sampling is often needed to track down and isolate individual discharges once a potential discharge problem is encountered at an outfall. Many of the sample collection protocols discussed in this section can be applied for in-pipe sampling, although additional testing methods to track down sources are described in Chapter 13.

2. When to Collect Samples

Indicator samples should be collected during dry weather periods to avoid flowing outfalls caused by storm water or groundwater infiltration. While the traditional definition of dry weather has been 72 hours without rainfall, some communities have shortened this window to 48 hours to make sampling more practical. An exception to this rule is sampling to respond to hotline complaints, which should be conducted immediately. Time of day that sampling is conducted is particularly important when the suspected source is residential sewage. Peak water usage occurs in the morning and evening, therefore sampling in the early morning (i.e., beginning of the work day) is recommended in these situations. In some regions of the country, sampling should be scheduled to coincide with the seasons where shallow groundwater influence is minimal.

3. Sample Bottle Preparation

Most indicator samples are stored in a polyethylene plastic sample bottle that is opaque or clear. Sample bottles can be reused, but only if they are acid-washed between field visits. If bacteria samples are collected, a new 120 ml sealed sample bottle is needed for each sample. Samples requiring a preservative are addressed in element 5.

4. Protocols for Sample Collection

Sample collection should reduce the potential for contamination, and prevent the field crew from being exposed to harmful pollutants. Some considerations for sample collection include:

- Wear surgical gloves (unpowdered nytrile gloves are recommended to limit chances of contamination) when collecting the sample, and wash hands with sanitary wipes after the sample(s) is collected.

- Dry weather flows can be shallow, have low flow volumes, and be hard to reach. In some cases, alternative sample collectors may be used. A "dipper," consisting of a measuring cup at the end of a long pole, can be used to catch flows from the outfall. A pre-measured, cut-off plastic milk jug can be used to capture shallow flows from the pipe (see Figure G.1). In either case, make sure not to disturb any sediments or benthic growth in the pipe as a sample is taken. Also, be sure to rinse these alternative sample collectors three times with sample water before collecting the sample.

- Fill the bottle completely to the top (i.e., with the meniscus at the rim).

- Do not touch the inside of the lid or bottle.

- Add any needed preservative at the time of sample collection. (See Step 5).

- Label the bottle immediately. Ensure that samples stay at 4°C (40°F). On a hot day, put samples in an ice-filled cooler immediately, or carry "blue ice" in a backpack.

5. Sample Storage and Preservation

If the field crew cannot get the samples back for analysis within the same day, they will need to preserve the samples using the techniques outlined in Table G.1. Some suppliers and contract labs provide pre-packaged sample bottles that contain required preservatives. Each indicator parameter has a unique sample preservation technique and a maximum hold time for laboratory analysis.

> **Tip**
> When analyzing multiple parameters and preserving samples, the field crew may need to collect up to four samples at a site: one preserved with H_2SO_4, one preserved with HNO_3, one sealed new bottle preserved with Na_2SO_3 for bacteria, and one unpreserved.

Figure G.1: A dipper (a) is helpful when the outfall is hard to reach. A milk jug (b) can be used to collect samples from shallow flow.

Table G.1: Sample Preservation and Storage Requirements for Typical Outfall Monitoring Parameters *(Primary Source: APHA, 1998)*		
Parameter	**Preservation[3]**	**Maximum Hold Time[4]**
Ammonia	H_2SO_4 to pH<2 Refrigerate to 4°C	7 to 28 days
Boron	HNO_3 to pH<2	28 days to 6 months
Chlorine[1]	Not Applicable	15 minutes
Color	Refrigerate to 4°C	48 hours
Conductivity	Refrigerate to 4°C	28 days
Detergents – Surfactants[2]	None Required	48 hours
Bacteria (*E. coli*, Enterococci, Total Coliform)[2]	$Na_2S_2O_3$ in chlorinated waters Refrigerate to 4°C	6 to 24 hours
Fluoride	None Required	28 days
Hardness	HNO_3 or H_2SO_4 to pH<2	6 months
pH[1]	Not Applicable	15 minutes
Potassium[2]	HNO_3 to pH<2	28 days
Turbidity	Refrigerate to 4°C Store in the dark	24-48 hours

1. Indicates parameters that should be analyzed in the field.
2. Data for these parameters taken from the National Environmental Methods Index (www.nemi.gov)
3. Many contract labs will provide sample bottles with preservative already added.
4. For parameters with a range, the lower number is recommended by the reference, and the higher number is the regulatory requirement for sample storage.

6. Sample Labeling and Chain of Custody

The labeling and integrity of each sample are important parts of the sampling protocol. Program managers should develop a process to track the "chain of custody" from the time the sample is initially collected until it is analyzed and reported as data. The process limits errors resulting from mis-labeling, lost samples, and improper laboratory analysis. Table G.2 outlines the nine minimum elements of a chain of custody, recommended by APHA (1998).

Table G.2: Nine Elements of a Chain of Custody	
Element of Chain of Custody	**Description**
1. Sample Labels	Labels should include a unique ID, type of sample, name of collector, date and time of collection, date and time of preservation, and preservative used (if applicable).
2. Sample Seals	Seals the lid on the label to ensure they are not tampered with.
3. Field Log Book	Includes basic information about sample collection, usually the Outfall Reconnaissance Inventory (ORI) field form can be used for this purpose.
4. Chain-of-Custody Record	A sheet that tracks the transfer of samples between individuals.
5. Sample Analysis Request Sheet	A sheet that requests specific analysis types from the laboratory.
6. Sample Delivery to the Laboratory	Ensure that sample delivery is timely. Include chain of custody records with the sample.
7. Receipt and Logging of Sample	The lab needs to document time of receipt of the sample
8. Assignment of Sample for Analysis	The lab supervisor assigns an analyst to the sample. The lab supervisor or analyst is responsible at this point.
9. Disposal	Save samples until results are confirmed and finalized. Dispose of according to US EPA approved methods.

7. Quality Assurance Measures During Sample Collection

To ensure sampling results are accurate, it is important to institute quality assurance measures as part of the sampling protocol. Quality assurance samples serve as a check against biases introduced during sample collection, or within the laboratory. Quality assurance samples also assess the accuracy of the analysis method and its consistency for samples collected at the same site. The sampling protocol should define a minimum fraction of samples that will be used for quality assurance purposes (typically about 5% - 10% of all samples collected). Examples of quality assurance samples include field blanks, duplicate samples, split samples and spiked samples, which are described below:

Field Blanks – Field blanks are deionized water samples prepared in the field at the time of sample collection. If the lab results for field blanks have non-zero values, it indicates that impurities were introduced to the sample during collection or lab analysis. The distilled deionized water should be placed in whatever is used to collect samples (e.g., sample scoop, dipper, plastic milk bottle) and then poured in the sample bottle, just as if it had been scooped or dipped as a real sample.

Duplicate (Replicate) Samples – This quality assurance technique relies on the collection of two or more samples from the same location and flow source during the same field visit. A discrepancy between the two sample measurements indicates a lack of precision or repeatability introduced during sample collection or lab analysis.

Field Spikes – A field spike is a sample to which a known concentration of an indicator parameter is added (e.g., an ammonia concentration of 1.0 mg/L). Any difference between the known concentration and the final laboratory measurement reveals errors introduced during sampling and laboratory analysis.

Split Samples – Splits consist of a single field sample that is divided into two separate sub-samples for subsequent laboratory analysis. Typically, split samples are submitted to different laboratories, or analyzed by different analysts to determine the precision of laboratory results. Alternatively, split samples can be analyzed at a single laboratory without knowledge of the sample origin (referred to as a “blind sample”). Any discrepancy between the two sub-samples suggests a lack of precision or repeatability introduced during sample collection or lab analysis.

8. Safety Considerations

Whenever sampling is done there are safety considerations that require planning. This is even more important when sampling is being conducted in urban stream environments where there is potential for contact with contaminated water, sharp debris and objects, and threatening individuals (both animals and humans). Field crews should be comprised of at least two individuals, each equipped with proper foot (e.g., sturdy boots or waders) and hand wear (latex gloves). Key equipment for crews to carry include cell phones, a list of contact and emergency numbers, a gps unit, and a first aid kit. Private properties should not be accessed unless proper notification has been provided, preferably in advance. Lastly, program managers may want to consider requiring/recommending field crews to be vaccinated against Hepatitis B, particularly if the crews will be accessing waters known to be contaminated with illicit sewage discharges.

References

American Public Health Association (APHA).1998. *Standard Methods for the Examination of Water and Wastewater – 20th Edition*. Washington, D.C.